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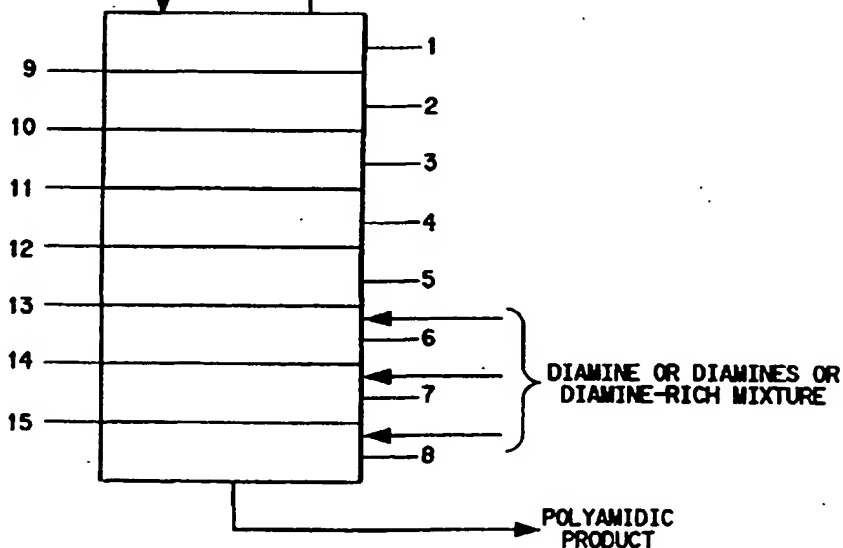
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(54) Title: CONTINUOUS POLYMERIZATION PROCESS FOR POLYAMIDES

(57) Abstract

The invention provides a continuous process for the preparation of polyamides, equipment in which the polymerization process can be conducted, and process control methods for said polymerization process.

TITLE

CONTINUOUS POLYMERIZATION PROCESS FOR POLYAMIDES

BACKGROUND

This invention concerns a continuous process for
5   the preparation of polyamides, the apparatus in which
the polymerization process can be conducted, and process
control methods useful in said polymerization process.

TECHNICAL BACKGROUND

Some commercially important polyamides, referred to
10 herein as dimonomeric polyamides, require starting
monomers of two kinds, one monomer having a pair of
carboxylic acid functional reactive groups(diacid) and
the other monomer having a pair of amino functional
reactive groups (a diamine). This class of polyamide
15 may incorporate more than one diacid and more than one
diamine and may incorporate a small amount, usually no
more than 10%, of a third kind of starting material
having a carboxylic acid functional group and an amino
functional group or a functional precursor to such a
20 compound. In the most common method of preparing
dimonomeric polyamides, the starting diacid and diamine
components are mixed in stoichiometric proportions into
a solution containing a large amount of water, typically
up to as much weight as the combined weight of the
25 diacid and diamine components. This water is
subsequently removed by evaporation which requires a
correspondingly large amount of energy. The evaporation
of water is usually done at elevated pressure in order
to achieve a high enough boiling temperature to prevent
30 the formation of solids. After the evaporation, there
must be a pressure reduction step which requires
excessive heat to prevent the product from solidifying.
The heating is known to cause discoloration and chemical
degradation of the product.
35   Attempts to produce dimonomeric polyamides without
the use of water or other solvents have usually been
unsuccessful. If one component is a solid, it is
difficult to accurately proportion the solid component.

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If both components are supplied as liquids (melt), these liquids may experience degradation, as a result of the high temperature supplied to keep the components in melt form.

5   United States Patent No. 4,131,712, endeavors to overcome these difficulties. This patent teaches a process for the preparation of a high molecular weight polyamide, wherein a diacid-rich component and a diamine-rich component are prepared separately in non-

10   stoichiometric proportions and then the diacid-rich component and the diamine-rich component are contacted in liquid state at a high enough temperature to prevent solidification, and in proportions such that the total amounts of diacid and diamine, whether combined or not,

15   are as much as possible stoichiometric. The major utility of the process is in the manufacture of nylon 66.

        One difficulty that is encountered as a result of the process in U.S. 4,131,712, where diamine or diamine

20   rich feed is added directly to a reactive polymerizing mixture, is that there is substantial volatilization of the diamine at the reaction temperature, especially during the last step of the process where the proportions of diacid and diamine approach

25   stoichiometric levels and the temperature is the highest. Means are required to prevent the escape of diamine and retain it in the reaction mixture in order to avoid loss of yield and to maintain stoichiometric balance.

30   U.S. Patents 4,433,146 and 4,438,257, teach the use of a partial condenser to condense diamine out of vapor leaving the reaction mixture so as to return the diamine to the reaction mixture. However, the procedure, if used on a commercial scale, with stepwise addition of

35   diamine, appears to require extended periods of time to recycle the diamine.

        U.S. Patent No. 5,155,184 discloses a process for the control of product composition during the

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manufacture of a polymer, employing near infrared
spectroscopy for detecting composition and using a
process computer. The disclosure relates to
polyolefins; no polyamide polymers are discussed
5   therein.

SUMMARY OF THE INVENTION

The present invention provides a continuous process
for the preparation of polyamides, of the group made by
joining of one or more diamines with one or more
10   diacids, for example nylon 66. This continuous process
has advantages over conventional processes by requiring
lower energy consumption, reduced capital cost of
equipment, reduced environmental emissions and cost
advantages pertaining thereto, and improved product
15   quality. In the process, a process stream of diacid or
diacid mixed with diamine is fed, as a molten liquid,
into the first stage of a multi-stage reactor and
additional diamine is fed into the reactor at one or
more of the additional stages. In a vertical reactor,
20   where the first stage is at the top, these additional
stages are lower than the first stage of the reactor.

More specifically, this invention provides a
continuous process for the manufacture of dimonomeric
polyamides, essentially without emission of diamine in
25   the vapor, which process comprises the steps of:

a) providing to a first reaction stage of a
multistage reactor, operating at a pressure which can
conveniently be essentially atmospheric, a process
stream comprising a molten diacid or a molten acid-rich
30   mixture comprising a dicarboxylic acid and a diamine;

b) flowing said process stream through a
series of the first reaction stage and at least one more
reaction stage;

c) adding to said process stream, in at least
35   one reaction stage beyond the first reaction stage, an
additional diamine component as either a vapor or a
diamine rich liquid; and

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d) optionally controlling the balance of acid and amine functional reactive groups (ends) in the resulting dimonomeric polyamide by an appropriate control system.

5   This invention includes the process above wherein there is also an optional control to maintain column stability using an appropriate column stability control system.

The reaction is conducted in a reaction apparatus
10   equipped with internals provided to cause effective contact of countercurrently flowing diamine or diamine-rich vapor with the molten acid or acid-rich feed stream so as to achieve rapid, efficient scrubbing of the diamine from the countercurrently flowing vapor,
15   providing that the temperature of the first stage and any further stages is sufficiently high to keep solid from forming in the reaction apparatus. It is preferred if the multistage reactor is vertical, with the top stage being the first stage.

20   This invention can be used to manufacture nylon 66 (poly-hexamethylene adipamide) where the starting materials are molten adipic acid or a molten adipic acid rich mixture of adipic acid and hexamethylene diamine. The acid rich mixture is about 75% to 85% by weight
25   adipic acid and about 15%-25% by weight hexamethylene diamine. The acid rich mixture is preferably about 81% by weight adipic acid and about 19% by weight hexamethylene diamine. In a preferred embodiment the process is carried out in a vertical multistage reactor,
30   having a first stage and one or more additional stages, typically six to eight stages. Hexamethylene diamine is added either as a vapor or a hexamethylenediamine rich liquid to at least one of the reaction stages beyond the first stage. The balance of acid and amine functional
35   reactive groups (ends) in the resulting polyamide is monitored and controlled by an appropriate control system.

In step d) it is preferred that control is accomplished by a near infrared activated feedback control system which, on demand, causes the injection of an appropriately small amount of hexamethylene diamine
5   vapor into or near the bottom stage of the reaction system so as to essentially achieve acid-amine ends balance.

The reaction is conducted in a reaction apparatus equipped with internals, such as but not limited to
10   perforated plates, coils and agitators, so as to cause effective contact of countercurrently flowing diamine or diamine-rich vapor (e.g., hexamethylene diamine or hexamethylene diamine-rich vapor) with the molten acid-rich feed so as to achieve rapid, efficient scrubbing of
15   the diamine from the countercurrently flowing vapor. The temperature of the first stage and any further stages must be sufficiently high to keep solid from forming in the reaction apparatus.

The invention also concerns a continuous process
20   for preparing an essentially anhydrous mixture comprising adipic acid and hexamethylene diamine in a 75-85:15-25, preferably a 81:19, weight ratio comprising the steps of:

    (a)   heating a heat stable liquid to about
25   80°C,

    (b)   adding solid adipic acid,

    (c)   agitating at about 80°C, at typically 200 RPM, until a solution is obtained (typically about two hours),

30   (d)   adding hexamethylene diamine to reach the desired weight ratio of weight adipic acid:hexamethylene diamine,

    (e)   heating the mixture to from about 120°C to about 135°C, with agitation, while allowing any water
35   present to evaporate to form an essentially anhydrous molten acid-rich mixture comprising a ratio of 75-85:15-25, preferably 81:19, by weight adipic acid:hexamethylene diamine, and

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(f)   feeding adipic acid and hexamethylene
diamine in a 75-85:15-25, preferably 81:19, ratio to the
molten acid rich mixture at the same rate that molten
acid-rich feed is withdrawn.

5   This method of making an acid rich feed is
applicable to other diacid-diamine combinations in
addition to adipic/hexamethylene diamine.

         This invention also provides processing apparatus,
in which the process of the present invention is carried

10   out, comprising a vertical multistage reactor equipped
with internals, for example perforated plates, coils and
agitators, so as to cause effective contact of
countercurrently flowing vapor and liquid streams.

         This invention further provides a method of process

15   control, by which the process of the present invention
is controlled, which method comprises a near infrared
activated feedback control system which determines acid-
amine ends balance and, where needed, causes the
injection of an appropriately small amount of additional

20   diamine into or near the bottom or final stage of the
reaction system so as to essentially achieve acid-amine
ends balance.

                    DETAILS OF THE INVENTION

         The process can be used to produce a wide variety

25   of dimonomeric polyamides and copolyamides depending on
the choice of diacids and diamines.

         By "dimonomeric polyamide" herein is meant a
polyamide prepared by the condensation polymerization of
two monomers, a diacid and a diamine, for example,

30   nylon 66 which is a polyamide prepared from adipic acid
(1,6-hexanedioic acid) and hexamethylene diamine.

         The diacid component may be selected from
aliphatic, alicyclic or aromatic diacids, with the
proviso that a diacid be capable of being used in melt

35   form by itself or as a melt or as a dispersion in
combination with other diacids or as an acid-rich feed
with diamine at a temperature that avoids excessive
degradation of the diacid.   Specific examples of such

acids include glutaric acid, adipic acid, suberic acid, sebacic acid, dodecanedioic acid, 1,2- or 1,3-cyclo-hexane dicarboxylic acid, 1,2- or 1,3-phenylene diacetic acid, 1,2- or 1,3-cyclohexane diacetic acid, isophthalic

5   acid, terephthalic acid, 4-4'-oxybis (benzoic acid), 4,4'-benzophenone dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, and p-t-butyl isophthalic acid. The preferred dicarboxylic acid is adipic acid.

The diamine component is selected from the group

10   consisting of aliphatic, alicyclic or aromatic diamines. Specific examples of such diamines include hexamethylene diamine, 2-methyl pentamethylenediamine, 2-methyl hexa-methylene diamine, 3-methyl hexamethylene diamine, 2,5-dimethyl hexamethylene diamine, 2,2-dimethylpenta-

15   methylene diamine, 5-methylnonane diamine, dodeca-methylene diamine, 2,2,4- and 2,4,4-trimethyl hexa-methylene diamine, 2,2,7,7-tetramethyl octamethylene diamine, meta-xylylene diamine, paraxylylene diamine, diaminodicyclohexyl methane and C_2-C_{16} aliphatic diamines

20   which may be substituted with one or more alkyl groups. The preferred diamine is hexamethylene diamine.

An optional third starting material, having a carboxylic acid functional group and an amino functional group or a functional precursor to such a compound, may

25   be selected from 6-aminohexanoic acid, caprolactam, 5-aminopentanoic acid, 7-aminoheptanoic acid and the like.

If the diacid does not suffer excess degradation at a temperature around its melting point, it may be used

30   directly as the feed stream to the first stage of the reactor. If the diacid is combined with one or more diamines to produce an acid-rich feed stream, this may be done continuously or batch-wise, so long as a steady feed stream to the first stage of the reactor is

35   maintained.

The feed stream for the first stage of the reactor comprises a flowable molten diacid or a flowable molten diacid rich mixture comprising the selected diacid and

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diamine. In the case where the process is used for the
preparation of nylon 66, the feed stream for the process
comprises flowable molten adipic acid or a flowable
molten adipic acid rich mixture comprising adipic acid
5   and hexamethylene diamine. In a preferred embodiment
for the preparation of nylon 66, the flowable acid rich
mixture comprises a molten mixture comprising
approximately 81% by weight of adipic acid and
approximately 19% by weight of hexamethylenediamine.

10   The diamine or diamines that are fed to one or more
stages after the first stage of the reactor may be
supplied in the form of a liquid or vapor. If fed as a
liquid, they undergo substantial vaporization when they
come in contact with the hot polymerizing reaction
15   mixture. Pre-vaporization of the diamine feed system
removes some of the heat requirement from the reactor
and reduces the likelihood of time to time variation in
the amount of diamine vapor flow at various points in
the reactor.

20   Figure 1, described below, shows the internal
configuration of a multistage reactor. Standard
distillation columns are suitable devices for this
purpose except that the liquid residence time in the
stages is increased to give time for chemical reaction.
25   Mechanical agitation is provided to enhance the exchange
of components between vapor and liquid, to prevent zones
of stagnation in the reaction mixture which could lead
to gel formation, to facilitate heat transfer and to
yield greater time-wise uniformity of product.

30   The absorption of diamine into a reactive polymeric
liquid is found to be most rapid and complete when the
liquid is highly acid-rich and at a relatively low
temperature. The rate of transfer of diamine from vapor
into liquid is sufficiently rapid and complete, even
35   when the liquid is close to a balance of acid and amine
ends, and at a high enough temperature to keep high
molecular weight polymer molten so that a reactor with
six to eight stages is capable of producing balanced

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polymer and at the same time of retaining in the polymer essentially all of the diamine fed to the reactor.

In comparison with conventional processes, the advantages of the process of the present invention include lower energy consumption, due to the efficient utilization of the heat of the amidation reaction and due to avoiding the need to evaporate off large amounts of water; reduced capital cost of equipment; reduced environmental emissions, due to the efficient absorption of diamine vapor by the acid-rich liquid flow in the reactor; and improved product quality, due to the lower residence time of the polyamide at elevated temperature and to lower final processing temperature. This results in a lower thermal degradation index and reduces the extent of discoloration.

In some cases, and in the preferred case where nylon 66 is the product and adipic acid is the starting dicarboxylic acid, the diacid must be combined with one or more diamines into an acid-rich feed stream in order to secure a feed in which the diacid remains chemically stable. This may be done continuously or batch-wise, as long as a steady feed stream to the first stage of the reactor is maintained. One method is provided in U.S. 4,131,712, col. 2, lines 30-39, which patent is incorporated herein by reference. A preferred method is to carry out this process continuously by combining, at this same rate at which molten acid-rich feed is withdrawn, with agitation, at approximately 120-135°C, feed streams of solid, granular adipic acid and liquid hexamethylene diamine or hexamethylediamine solution (which is commercially used at 85-100% purity, balance being water). Holding time in the agitated reactor is approximately one to three hours. Holding for longer times is not detrimental to the reaction product.

A preferred method for preparing the acid-rich feed utilized in the preparation of nylon 6,6 in a continuous fashion comprises the steps of (a) heating a heat stable liquid to about 80°C, (b) adding solid adipic acid,

(c) agitating at about 80°C until a solution is obtained, (d) adding hexamethylene diamine to reach the desired 81:19 by weight adipic acid:hexamethylene diamine ratio, (e) heating the mixture to about 125°C to
5 135°C, preferably about 130°C, with agitation while allowing any water present to evaporate to form an essentially anhydrous molten acid-rich mixture comprising 81:19 by weight adipic acid:hexamethylene diamine, and (f) feeding adipic acid and hexamethylene
10 diamine in a 75-85:15-25 ratio, preferably a 81:19 ratio, to the molten acid rich mixture at the same rate that molten acid-rich feed is withdrawn.

The heat stable liquid is used to facilitate heat and mass transfer. Water or a stable molten diacid, for
15 example dodecanedioic acid, may be employed. Water is preferred.

Solid crystalline adipic acid is employed. Depending on particle size, time to reach solution state may vary. Typically, agitation at this step is 200 RPM
20 for 2 hours.

Hexamethylene diamine or hexamethylene diamine solution, which may contain up to about 15% water may be used. The amount of water to he evaporated varies. (For example, in cold weather, the diamine is shipped
25 with about 20% water.) If water is employed as the heat stable liquid and hexamethylene diamine solution is used, water to be removed is at a maximum. If a stable molten diacid, for example, dodecanedioic acid, is employed as the heat stable liquid, water removal is
30 minimized.

Essentially anhydrous in the present context means approximately 2% water or less. If a heat stable liquid other than water is used, for example, dodecanedioic acid, once the continuous feed of adipic acid and
35 hexamethylene diamine in an 81:19 ratio to the molten acid rich mixture is commenced, some time will be required before steady state operation is reached. That is, some time will be required before the heat stable

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liquid other than water is diluted out of the acid-rich feed mixture.

        If continuous operation is suspended after step (f) of the process is reached, the mixture may be cooled and
5 reheated and operation recommenced without ill effect without having to repeat steps (a) though (e).

        In a most preferred mode, the exit stream from the acid rich mixture makeup vessel to the first stage of the reactor is continuously monitored by near infrared
10 spectrophotometry. The near infrared analysis predicts percent adipic acid. Measurement is done in line and continuously, as the material flows through the reactor feed pipe. Based on this analysis, changes are made continuously in the hexamethylene diamine (HMD) feed
15 rate. A computer causes the HMD injection to respond to bring the composition closer to the set point.

        To produce a product with time-wise uniformity suitable for commercial end uses, it is necessary to monitor and control the difference between the
20 concentration of the carboxylic acid functional end groups and the concentration of amine functional end groups in the resulting dimonomeric polyamide by an appropriate control system. This requirement is especially stringent for product that will eventually be
25 formed into fibers that will be treated with dyes that attach themselves to one or the other of the two functional groups.

        To achieve this control a measurement is made of some characteristic in the polymer leaving the final
30 stage of the reactor which is sufficiently sensitive to the concentration difference. The method must be accurate to within about plus or minus 0.5 units in the difference in acid and amine ends concentrations (gram equivalent ends per million grams of polymer). Any
35 analytical method of this approximate accuracy, that is rapid enough to give answers in a timely enough fashion to effect process control, would be suitable. In general, manual titrimetric methods, though sufficiently

accurate, are not rapid enough to give meaningful
process control. A preferred method of monitoring
reactor output is by near-infrared spectrophotometry.
The near-infrared analysis measures the difference
5   between acid and amine ends to an acceptable degree of
accuracy with a sufficiently timely response. Based on
this analysis, changes are made in the hexamethylene
diamine feed into or near the bottom stage of the
reactor system. By "into or near" is meant that this
10   feed is into the bottom reactor stage, into the stage
immediately above the bottom stage or into the transfer
line leading out of the bottom reactor stage. Most
preferably, this feed is into the transfer line.

The desired product from the transfer line is
15   generically described, in the case of nylon 6,6
processing, as intermediate molecular weight nylon. As
such it is suitable for sale as is, or it can be further
processed to higher molecular weight nylon by methods
known in the art, for example, in an extruder or through
20   solid phase polymerization.

DESCRIPTION OF THE DRAWINGS

Figure 1 describes diagramatically the internal
configuration of a reactor. The reactor is divided into
discrete stages 1-8 using perforated barriers, 9-15,
25   between stages, which barriers allow separate passages
for vapor and liquid flows from stage to stage.

Figure 2 describes an eight stage reactor. Feed
material streams 16 and 17 are fed into mix tank 18 for
diacid rich feed preparation. The acid rich mixture is
30   then fed into stage 1. The column is heated by heat
sources 19-24. Agitator 30 is located at the bottom of
the reactor. Hexamethylene diamine vapor is fed into
the acid rich mixture at various stages 2 through 8.
Nylon 66 polymer is removed after bottom stage 8.
35   Beyond the first stage, each stage is separated from the
stage above and below it by a horizontal perforated
barrier 25 with openings 26 and 27, respectively, for
liquid and vapor to flow through. Liquid flowing from

the bottom stage 8 is continuously removed at the bottom of the reactor.

5   Vapor of hexamethylene diamine is supplied continuously into the upper part of each of three stages above the bottom stage. This vapor and any additional vapor of diamine or steam formed within the reactor flows from each stage to the stage above through a multiplicity of small holes in barrier 25, thus bringing the vapor into intimate contact with the liquid in the
10 stage above. Vapor flowing through the top stage is continuously removed from the top of the reactor. Heat may be supplied at each stage by means of heat sources 19-24 to prevent the formation of solid material.

EXAMPLES

15 ### Near-Infrared Monitoring: Pre-polymer Method I

In monitoring the exit stream from the column, the goal is to first measure then control the ends balance and the conversion. In the case of the preferred embodiment, the preparation of nylon 66, the ends
20 balance and the conversion are specified by determining any two of the following: amine ends concentration ($[A]$), carboxyl ends concentration ($[C]$), difference of ends (DE or $[C]-[A]$) and sum of ends (SE or $[C]+[A]$). Polymer relative viscosity (RV) can be used in place of
25 sum of ends. The analysis and control may be carried out essentially continuously.

In a demonstration of the preferred process, the preparation of nylon 66, near-infrared spectra of the pre-polymer melt were obtained using a UOP/Guided Wave
30 Model 300P near-infrared spectrometer. A pair of 5.5" x 0.25" diameter sapphire-windowed optical transmission probes (UOP/Guided Wave), available from UOP/Guided Wave, El Dorado Hills, CA, were inserted directly into the exit stream of the column using a NIR cell located
35 at the exit of the column. The NIR cell consisted of a block of 316 stainless steel through which perpendicular holes had been drilled; the pre-polymer melt flowed through a 5 mm diameter channel the length of the cell;

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the GW probes were inserted perpendicular to the flow
and held in place with Conax® fittings manufactured by
Conax Buffalo Corp., 2300 Walden Avenue, Buffalo, NY
14225 and Kalrez® (DuPont) seals. The optical

5 pathlength between the probes was about 5 mm. Two flat
band-heaters were placed around the block cell. The
probes were connected to the spectrometer using
20 meters of jacketed 500 micron single fiber optic
cable (UOP/Guided Wave).

10   During a three day test run, the near-infrared
monitoring system was programmed to automatically scan
and save an absorbance spectrum (the average of 8 scans)
of the pre-polymer melt once every five minutes. At
roughly fifteen minute intervals, discrete samples were

15 taken at the exit of the column (a few inches beyond the
NIR cell). The samples were analyzed by titration to
determine the acid and amine end concentrations, [C] and
[A]. See Volume 17 of the "Encyclopedia of Industrial
Chemical Analysis" published by John Wiley and Sons

20 (1973), page 293. The lab results were reported as acid
and amine ends, in meq ends/kg polymer, to the nearest
0.1 end.

      At the conclusion of the test, the NIR spectra
nearest (within 5 minutes) in time to each of the lab

25 samples collected were extracted from the spectra in the
data set to give a calibration set of 26 samples. The
calibration set spanned a range of 100 to 400 amine ends
and 50 to 170 acid ends. The calibration spectra were
smoothed and baseline corrected using Scanner 300

30 software supplied with the UOP/Guided Wave spectrometer.

      Partial least squares (PLS) models were developed
using the wavelength region between 1000 and 2100 nm.
PLS models were developed using the Unscrambler® (Camo
A/S, Trondheim, Norway) chemometrics software package

35 following the directions supplied by the vendor. The
use of PLS models is widely known and taught in the open
literature.

For amine ends, a two-factor PLS model explained
98.0% of the X-variance and 97.2% of the Y-variance in
the calibration set. It predicted the pre-polymer
composition with an accuracy (SEP) of 15.8 amine ends
5   and a correlation coefficient (R) of 0.987.

This calibration set did not contain sufficient
variation to independently model acid ends.

Validation was done by predicting composition data
with this model in real time during subsequent unit
10 operations. The model predictions were converted using
an empirical linear equation from amine ends ([A]) to
difference of ends (DE) for operator convenience, since
it was found that over the short term, the amine ends
values and the difference of ends values were highly
15 correlated. The resulting DE predictions tracked the
lab results (although with an offset that changed
periodically), responded correctly to known process
changes, and had a repeatability (standard deviation of
consecutive predictions) of 1.3 ends over an hour and
20 0.95 ends over a ten minute period.

The model obtained in this manner was used to
control the composition of the pre-polymer melt.
Depending on the value of DE obtained, and the desired
value, changes in the column operation were made.
25   Near-Infrared Monitoring: Pre-polymer Method II

In monitoring the exit stream from the column, the
goal is to first measure then control the ends balance
and the conversion. In the case of the preferred
embodiment, the preparation of nylon 66, the ends
30 balance and conversion are specified by determining any
two of the following: amine ends concentration ([A]),
carboxyl ends concentration ([C]), difference of ends
(DE or [C]-[A]) and sum of ends (SE or [C]+[A]).
Polymer reactive viscosity (RV) can be used in place of
35 ends. The analysis and control may be carried out
essentially continuously.

In a demonstration of the preferred process, the
preparation of nylon 66, near-infrared spectra of the

pre-polymer melt were obtained using a UOP/Guided Wave
Model 300P near-infrared spectrometer. A pair of 5.5" x
0.25" diameter sapphire-windowed optical transmission
probes (UOP/Guided Wave) were inserted into sapphire-
5   windowed stainless steel "sleeves" in a NIR cell located
in the transfer line following the column. The probes
did not directly contact the pre-polymer melt. The cell
was heated by hot oil. The optical pathlength between
the probes was 5 mm. The probes were connected to the
10   spectrometer using about 100 meters of jacketed
500 micron single fiber optic cable (UOP/Guided Wave).

The near-infrared monitoring system was programmed
to automatically scan and save an absorbance spectrum
(the average of 8 scans) of the pre-polymer melt once
15   every fifteen minutes. Once an hour discrete samples
were taken at the pelletizer at the end of the transfer
line. The samples were analyzed by titration to
determine the difference of ends, DE, and the amine end
concentration, [A]. The lab results were reported in
20   meq ends/kg polymer or "ends" to the nearest 0.1 end.

Over a four day period, the NIR spectra nearest
(within 5 minutes) in time to each of the lab samples
collected were extracted from the spectra in the data
set to give a calibration set of 67 samples. The
25   calibration set spanned a range of -167.0 to +81.0
difference of ends and 33.0 to 221.4 amine ends. The
calibration spectra were smoothed and baseline corrected
using Scanner 300 software supplied with the UOP/Guided
Wave spectrometer.
30   Partial least squares (PLS) models were developed
using the wavelength region between 1504 nm and 1576 nm.
The PLS model was developed using the Unscrambler® (Camo
A/S, Trondheim, Norway) chemometrics software package
following the directions supplied by the vendor. The
35   use of PLS models is widely known and taught in the open
literature.

For difference of ends, a two-factor PLS model
explained 99.1% of the X-variance and 95.2% of the

Y-variance in the calibration set. It predicted the
pre-polymer composition with an accuracy (SEP) of 13.3
ends and a correlation coefficient (R) of 0.977.

This calibration set did not contain sufficient
5   variation to independently model sum of ends.

Validation was done by predicting composition data
with this model for a different two day period. The
model predictions tracked the lab results (though with
an offset that changed periodically) and had a
10   repeatability (standard deviation of consecutive
predictions) of 1.5 ends over an hour and 0.50 ends over
a ten minute period.

A model obtained in a similar manner was used to
control the composition of the pre-polymer melt.
15   Depending on the value of DE obtained, and the desired
value, changes in the column operation were made.

Near-Infrared Monitoring: Acid-rich Feed

In monitoring the exit stream from the acid-rich
makeup vessel (also referred to herein as acid-rich feed
20   ARF), the goal is to first measure then control the
chemical composition (the relative amount of diacid and
diamine components). In the case of the preferred
embodiment, the preparation of nylon 66, this is
conveniently expressed as weight percent adipic acid.
25   If the preparation of the acid rich mixture is carried
out in a continuous fashion, the analysis and control
can also be carried out essentially continuously.

In a demonstration of the preferred process, the
preparation of nylon 66, near-infrared spectra of the
30   ARF were obtained using a UOP/Guided Wave Model 300P
near-infrared spectrometer. A pair of 5.5" x 0.25"
diameter sapphire-windowed optical transmission probes
(UOP/Guided Wave) were inserted directly into the 0.25"
tubing exit stream of the acid-rich feed unit using a
35   Swagelok® cross, available from Swagelok Co., Solon, OH
44139 and two Conax® fittings, equipped with Viton®
O-ring seals, both available from Conax Buffalo Corp.,
2300 Walden Avenue, Buffalo, NY 14225. The optical

pathlength between the probes was about 5 mm. The
probes were connected to the spectrometer using
20 meters of jacketed 500 micron single fiber optic
cable (UOP/Guided Wave).

5   During a two day test run the ARF composition was
varied stepwise from 77% adipic acid to 85% adipic acid.
The near-infrared monitoring system was programmed to
automatically scan and save an absorbance spectrum (the
average of 8 scans) of the ARF once every five minutes.

10 At roughly half-hour intervals, discrete samples were
taken at the exit of the ARF unit (a few inches beyond
the NIR probes). The samples were analyzed by
titration. Twenty five grams of acid-rich feed were
dissolved in 325 mL of water at 25°C. The solution was

15 titrated with a 50% by weight solution of hexamethylene
diamine in water to a potentiometric endpoint of
7.600 pH. (The calculations assumed a sample moisture
level of 2.0% and no conversion of diacid and diamine to
nylon 66 pre-polymer.) The lab results were reported as

20 weight percent adipic acid (dry basis) to the nearest
0.1%.

     At the conclusion of the test, the NIR spectra
nearest (within 5 minutes) in time to each of the lab
samples were extracted from the spectra in the data set

25 to give a calibration set of 57 spectra. The
calibration spectra were smoothed and baseline corrected
using Scanner 300 software supplied with the UOP/Guided
Wave spectrometer.

     Partial least squares (PLS) models were developed

30 using the wavelength region between 1000 nm and 1670 nm.
The PLS models were developed using the Unscrambler®
(Camo A/S, Trondheim, Norway) chemometrics software
package following the directions supplied by the vendor.
The use of PLS models is widely known and taught in the

35 open literature. A two-factor PLS model explained 99.6%
of the X-variance and 97.3% of the Y-variance in the
calibration set. It predicted the ARF composition with

an accuracy (SEP) of 0.17% adipic acid and a correlation coefficient (R) of 0.989.

. Validation was done by predicting composition data with this model for the other obtained spectra. The
5   model predictions tracked the lab results, responded correctly to known process changes, and had a repeatability (standard deviation of consecutive predictions) of 0.03% adipic acid.

Further validation was done by predicting
10   composition data with this model in real time during a subsequent test run. During this run the model predictions tracked the lab results (although with an offset of about -0.6% adipic acid), responded correctly to known process changes, and had a repeatability of
15   0.02% adipic acid.

The model obtained in this manner was used to control the composition of the ARF. Depending on the value of % adipic acid obtained, and the desired value, changes in the reactant ratios were made.
20   EXAMPLE 1

A molten acid-rich mixture, consisting of 81% by weight of adipic acid and 19% by weight of hexamethylene diamine was supplied continuously to the top of a 4 inch diameter vertical reactor. The reactor was divided into
25   eight stages, each stage separated from the stage above and below it by a horizontal perforated barrier. Reactor temperature was controlled so that a temperature gradient existed, with the top stage held at 178°C and the bottom stage at 276°C. Liquid flowed from each
30   stage to the stage below it through an opening in the barrier that was fitted with a tube leading into and below the surface of the reaction mixture in the stage below. Liquid flowing through the bottom stage was continuously removed from the bottom of the reactor.

35   Vapor of hexamethylene diamine was supplied continuously into the upper part of each of three stages above the bottom stage. This vapor and any additional vapor of diamine or steam formed within the reactor

flowed from each stage to the stage above through a
multiplicity of small holes in the barrier, thus
bringing the vapor into intimate contact with the liquid
in the stage above. Vapor flowing through the top stage

5   was continuously removed from the top of the reactor.
Heat was supplied at each stage to prevent the formation
of solid material.

The liquid leaving the bottom of the vessel was
analyzed and found to have a carboxyl end content

10   between 69 and 156 gram equivalents per million grams of
sample, an amine end content of between 38 and 136, and
a Relative Viscosity of between 18 and 28 (as measured
at 25°C as a 8.4% by weight solution in a solvent
consisting of 90% formic acid and 10% water and compared

15   with the viscosity of the solvent at 25°C). Based on
the end group content, the number average molecular
weight of the polymer product was 10,500.

The vapor leaving the top of the reactor was
analyzed and found to contain less than 100 parts per

20   million by weight of hexamethylene diamine. This means
a loss of diamine of 0.000016 parts by weight per part
of polymer. Typical commercial processes for making
nylon 66 lose between 0.001 and 0.002 parts of diamine
per part of polymer produced.

25   EXAMPLE 2

A molten acid-rich mixture, consisting of 81% by
weight of adipic acid and 19% by weight of hexamethylene
diamine was supplied continuously to the top of a
vertical reactor at a rate of approximately 200 pounds

30   per hour. The reactor was 15.5 inches in internal
diameter and about 17 feet high. It was divided into
eight stages, each separated from the stage above and
below it by a horizontal perforated barrier. Liquid
flowed from each stage to the stage below through an

35   opening in the barrier that was fitted with a tube
leading into and below the surface of the reaction
mixture in the stage below. Liquid flowing through the
bottom stage was continuously removed from the bottom of

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the reactor. Vapor of hexamethylene diamine was
supplied continuously into the upper part of each of the
three stages above the bottom stage. Total flow of
diamine was approximately 89 pounds per hour. This
5   vapor and any additional vapor of diamine or steam
formed within the reactor flowed from each stage to the
stage above through a multiplicity of small holes in the
barrier, thus bringing it into intimate contact with the
liquid in the stage above. Vapor flowing through the
10   top stage was continuously removed from the top of the
reactor. Heat was supplied to each stage as required to
prevent the formation of solid material. The polymeric
material leaving the bottom of the reactor passed
through a length of pipe before being sampled. The
15   average residence time in the pipe was about six
minutes, which provided time for additional reaction in
the liquid. The liquid leaving the end of the pipe was
analyzed and found to have an average carboxyl end
content of 111.5 (plus or minus 20) gram equivalents per
20   million grams of sample, an average amine end content of
71 (plus or minus 13), and an average Relative Viscosity
of 25.1 (plus or minus 3); the RV was calculated based
on the sum of the carboxyl and amine ends using a
standard formula. Based on the end group content, the
25   number average molecular weight of the polymer product
was 10,960. These results were obtained during a period
of continuous operation of 31 hours.

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What is claimed is:

1.   A process for the manufacture of dimonomeric
polyamide which process comprises the steps of:

            a)   providing to a first reaction stage of a
5   multistage reactor, having a first stage and one or more
additional stages a process stream comprising a molten
diacid or a molten acid-rich mixture comprising a
dicarboxylic acid and a diamine;

            b)   flowing said process stream through a
10 series of a first reaction stage and at least one more
reaction stage;

            c)   adding to said process stream, in at
least one of the reaction stages beyond the first
reaction stage, an additional diamine component as
15 either a vapor or a diamine rich liquid;

            d)   controlling the balance of acid and amine
ends in the resulting dimonomeric polyamide by an
appropriate control system; and

            e)   maintaining the temperature of the first
20 reaction stage and any further stages at a sufficiently
high temperature to keep solid from forming in the
reaction apparatus.

      2.   The process of Claim 1 wherein the multistage
reactor is equipped with internals to cause effective
25 contact of any countercurrently flowing diamine or
diamine-rich vapor with the molten acid or acid-rich
process stream.

      3.   The process of Claim 1 wherein the product
manufactured is poly(hexamethylene adipamide),
30 (nylon 66), and wherein the process stream of step (a)
comprises molten adipic acid or a molten adipic acid-
rich mixture comprising adipic acid and hexamethylene
diamine and the additional diamine component added in
step (c) is hexamethylene diamine added either as a
35 vapor or a hexamethylenediamine rich liquid.

      4.   The process of Claim 2 wherein the product
manufactured is poly(hexamethylene adipamide),
(nylon 66), and wherein the process stream of step (a)

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comprises molten adipic acid or a molten adipic acid-
rich mixture comprising adipic acid and hexamethylene
diamine and the additional diamine component added in
step (c) is hexamethylene diamine added either as a
5   vapor or a hexamethylenediamine rich liquid.

     5.   The process of Claim 3 wherein the multistage
reactor is vertical and wherein the molten acid-rich
mixture of step (a) comprises approximately 81% by
weight of adipic acid and approximately 19% by weight of
10   hexamethylene diamine.

     6.   The process of Claim 4 wherein the multistage
reactor is vertical and wherein the molten acid-rich
mixture of step (a) comprises approximately 81% by
weight of adipic acid and approximately 19% by weight of
15   hexamethylene diamine.

     7.   The process of Claim 1 or Claim 2 conducted at
essentially atmospheric pressure.

     8. The process of Claims 1 or 2 wherein the
control system of step (d) is a near infrared activated
20   feedback control system which, on demand, injects an
appropriately small amount of hexamethylene diamine
vapor into or near the bottom stage of the reaction
system so as to essentially achieve acid-amine ends
balance.

25   9.   The process of Claim 1 or Claim 2 wherein the
diacid is selected from the group consisting of
aliphatic, alicyclic or aromatic diacids.

    10.   The process of Claim 9 wherein the diacid is
selected from glutaric acid, adipic acid, suberic acid,
30   sebacic acid, dodecanedioic acid, 1,2- or 1,3-cyclo-
hexane dicarboxylic acid, 1,2- or 1,3-phenylene diacetic
acid, 1,2- or 1,3-cyclohexane diacetic acid, isophthalic
acid, terephthalic acid, 4,4-oxybis (benzoic acid),
4,4-benzophenone dicarboxylic acid, 2,6-naphthalene
35   dicarboxylic acid and p-t-butyl isophthalic acid.

    11.   The process of Claim 10 wherein the diacid is
is adipic acid.

12.   The process of Claim 1 wherein the diamine
component is selected from the group consisting of
aliphatic, alicyclic or aromatic diamines.

13.   The process of Claim 12 wherein the diamine is
5   selected from the group consisting of hexamethylene
diamine, 2-methyl pentamethylenediamine, 2-methyl
hexamethylene diamine, 3-methyl hexamethylene diamine,
2,5-dimethyl hexamethylene diamine, 2,2-dimethyl-
pentamethylene diamine, 5-methylnonane diamine,
10   dodecamethylene diamine, 2,2,4- and 2,4,4-trimethyl
hexamethylene diamines, 2,2,7,7-tetramethyl
octamethylene diamine, meta-xylylene diamine,
paraxylylene diamine, diaminodicyclohexyl methane and
C_2-C_{16} aliphatic diamines, optionally substituted with
15   one or more alkyl groups.

14.   The process of Claim 13 wherein the diamine is
hexamethylene diamine (HMD).

15.   Apparatus comprising a vertical multistage
reactor having a first stage and at least one additional
20   stage equipped with internals, perforated plates, coils
and agitators, to cause effective contact of
countercurrently flowing vapor and liquid streams.

16.   A method of process control comprising a near
infrared activated feedback control system which, on
25   demand, injects an appropriately small amount of
hexamethylene diamine vapor into or near the bottom
stage of a reaction system so as to essentially achieve
acid-amine ends balance.

17.   A continuous process for preparing an
30   essentially anhydrous mixture comprising adipic acid and
hexamethylene diamine in a 75-85:15-25 weight ratio
comprising the steps of:

(a) heating a heat stable liquid to about
80°C,

35   (b) adding solid adipic acid,

(c) agitating at about 80°C until a solution
is obtained,

(d) adding hexamethylene diamine to reach the desired 75-85:15-25 by weight adipic acid:hexamethylene diamine ratio,

(e) heating the mixture to about 120°C to
5   about 135°C, with agitation, while allowing any water present to evaporate to form an essentially anhydrous molten acid-rich mixture comprising 75-85:15-25 by weight adipic acid:hexamethylene diamine, and

(f) feeding adipic acid and hexamethylene
10   diamine in an 75-85:15-25 ratio to the molten acid rich mixture at the same rate that molten acid-rich feed is withdrawn.

18.   The process of Claim 17 wherein the ratio of adipic acid to hexamethylene diamine in the molten acid-
15   rich mixture in step (e) is 81:19 and the ratio of adipic acid to hexamethylene diamine feed in (f) is 81:19.

19.   Process of Claim 1 wherein the molten acid-rich mixture is provided in a continuous process.
20   20.   The process of Claim 19 wherein the continuous process is the process of Claim 17.
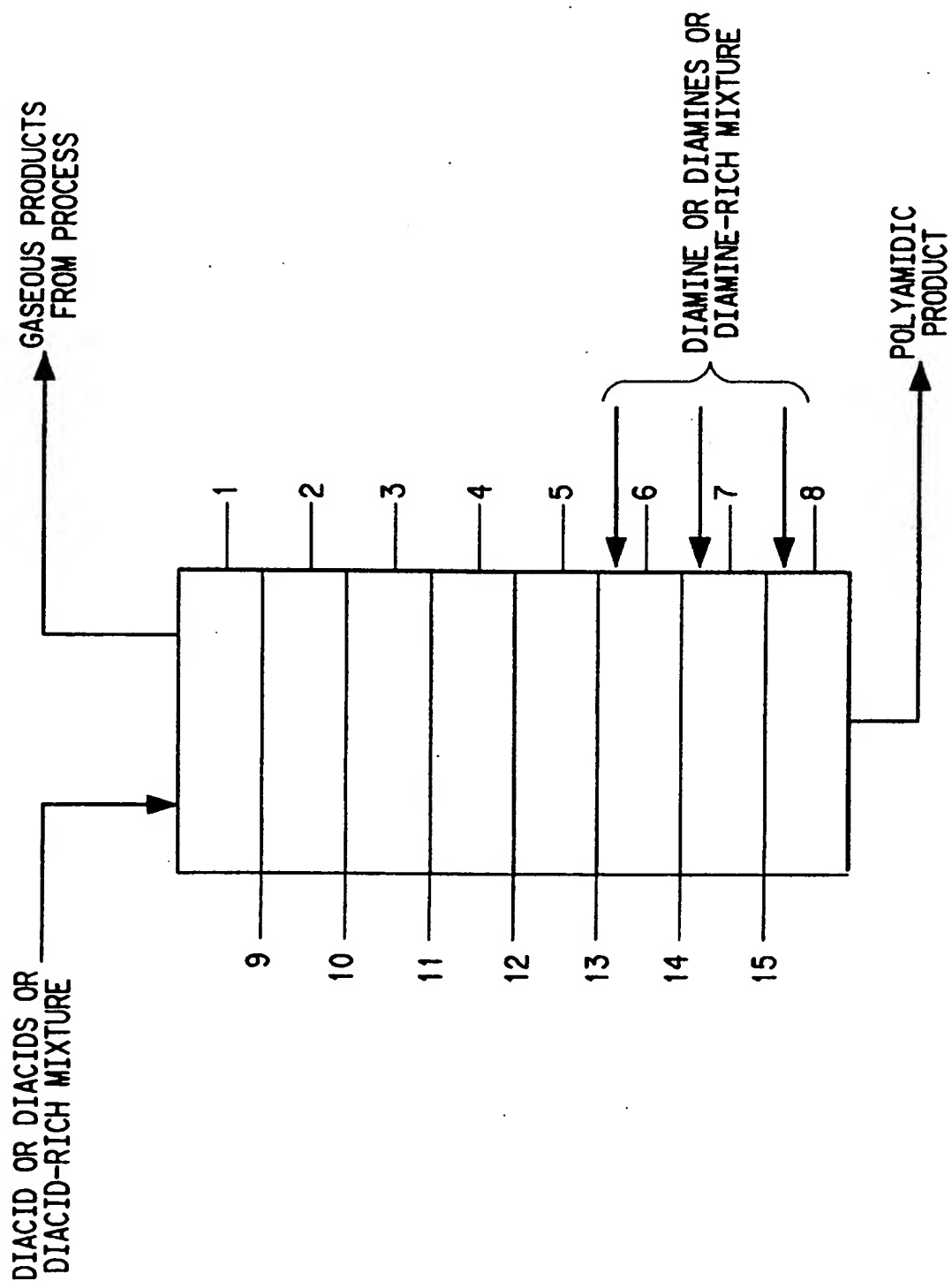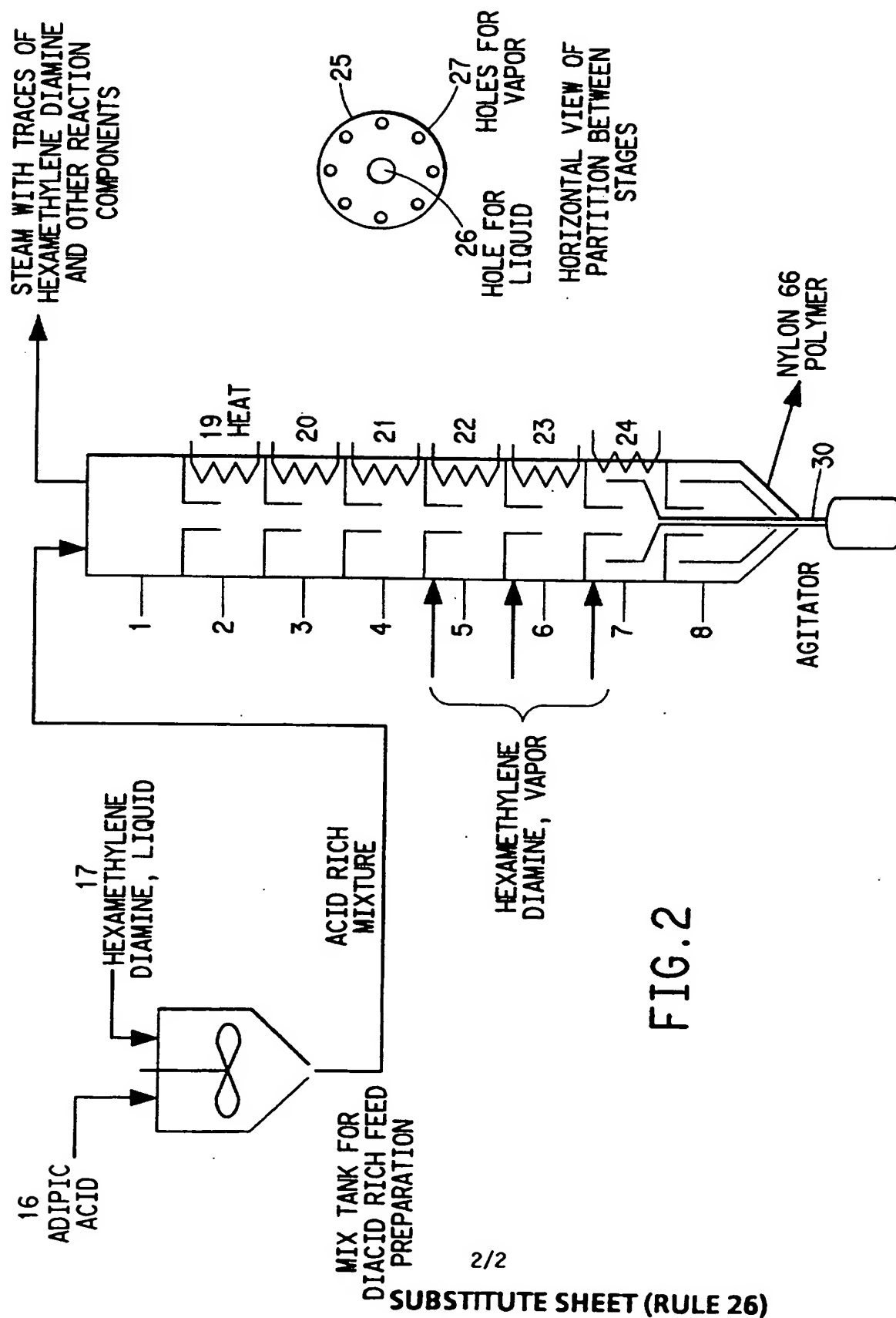
FIG. 1

SUBSTITUTE SHEET (RULE 26)

STEAM WITH TRACES OF HEXAMETHYLENE DIAMINE AND OTHER REACTION COMPONENTS

25
27 HOLES FOR VAPOR
26 HOLE FOR LIQUID

HORIZONTAL VIEW OF PARTITION BETWEEN STAGES

19 HEAT
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NYLON 66 POLYMER
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AGITATOR

17 HEXAMETHYLENE DIAMINE, LIQUID

ACID RICH MIXTURE

HEXAMETHYLENE DIAMINE, VAPOR

16 ADIPIC ACID

MIX TANK FOR DIACID RICH FEED PREPARATION

FIG.2

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INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C08G69/28   C08G69/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 131 712 (SPRAUER JEROME W) 26 December 1978 cited in the application -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 April 1996	24. 04 96

Name and mailing address of the ISA	Authorized officer
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